



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 1 365 000 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
26.11.2003 Bulletin 2003/48

(51) Int Cl.7: **C09K 3/18, C08F 2/24,
D06M 15/277**

(21) Application number: **02716432.6**

(86) International application number:
PCT/JP02/00624

(22) Date of filing: **29.01.2002**

(87) International publication number:
WO 02/064696 (22.08.2002 Gazette 2002/34)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

• **YOSHIOKA, T.,
Yodogawa Works of DAIKIN IND., LTD
Settsu-shi, Osaka 566-8585 (JP)**
• **KASHIWAGI, M.,
Yodogawa Works of DAIKIN IND., LTD
Settsu-shi, Osaka 566-8585 (JP)**

(30) Priority: **30.01.2001 JP 2001021590**

(74) Representative: **HOFFMANN - EITLE
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)**

(71) Applicant: **DaiKin Industries, Ltd.
Osaka-shi, Osaka 530-8323 (JP)**

(72) Inventors:
• **KUBOTA, K.,
Yodogawa Works of DAIKIN IND., LTD
Settsu-shi, Osaka 566-8585 (JP)**

(54) WATER- AND OIL-REPELLENT COMPOSITION, PROCESS FOR PRODUCING THE SAME AND USE THEREOF

(57) Excellent water- and oil-repellency performances resulting from low temperature curing are achieved by an aqueous dispersion type fluorine-containing water- and oil-repellent composition containing a polymer of a perfluoroalkyl group-containing ethylenically unsaturated monomer dispersed in an aqueous

medium, wherein the composition contains a nonionic surfactant having an HLB value of at most 11 and a cationic surfactant, and a homopolymer of at least one monomer constituting the polymer has T_g of at most 50°C.

EP 1 365 000 A1

Description**FIELD OF THE INVENTION**

[0001] The present Invention relates to a water- and oil-repellent composition. Particularly, the present invention relates to an aqueous dispersion type water- and oil-repellent composition having the improved water- and oil-repellency under low temperature curing conditions.

BACKGROUND ART

[0002] An aqueous dispersion type fluorine-containing water- and oil-repellent is generally used. Various attempts have been made to improve properties obtained by curing at a low temperature. The polymer structures are devised in, for example, JP-B-63-67511 (a graft polymer comprising a diene monomer, ether group-containing (meth)acrylate and a fluoromonomer) and JP-A-10-237133 (fluoroalkyl acrylate (FA)/stearyl acrylate (StA)/chloroethyl vinyl ether/N-methylol acrylamide (N-MAM), etc.). However, the conventional procedures cannot give sufficient water- and oil-repellency obtained by curing at low temperature. In particular, it is difficult to impart sufficient properties to a polyolefin fiber.

[0003] JP-A-4-164990 discloses a composition comprising a nonionic surfactant having an HLB value of at most 10 in addition to a fluorine-containing cationic surfactant and a fluorine-free cationic surfactant. JP-A-4-164990 has the object of improving the dispersion stability, but does not disclose the improvement of the water-and oil-repellency properties.

[0004] The conventional aqueous dispersion type fluorine-containing water- and oil-repellent agents have insufficient water- and oil-repellency obtained by curing at low temperature. A water- and oil-repellent agent which can exhibit excellent water- and oil-repellency obtained by drying or heat-treatment at low temperature is desired. In particular, it is highly desirable to give the water- and oil-repellent agent imparting excellent water- and oil-repellency to a polyolefin fiber which has low heat-resistance of fiber itself and which cannot be cured at high temperature.

SUMMARY OF THE INVENTION

[0005] The present Inventors discovered that, when an aqueous dispersion type water-and oil-repellent agent comprising a homopolymer or copolymer of a perfluoroalkyl group-containing ethylenically unsaturated monomer dispersed in an aqueous medium contains a specified emulsifier having a low HLB value, the water- and oil-repellent agent can exhibit excellent performances even if the agent is cured at low temperature, and then completed the present invention.

[0006] That is, the present invention provides an aqueous dispersion type fluorine-containing water- and oil-repellent composition comprising a polymer of a perfluoroalkyl group-containing ethylenically unsaturated monomer dispersed in an aqueous medium, wherein the composition contains a nonionic surfactant having an HLB value of at most 11 and a cationic surfactant, and a homopolymer of at least one monomer constituting the polymer has a glass transition temperature (Tg) of at most 50°C.

[0007] Further, the present invention provides a method of producing said composition, a water- and oil-repelling treatment method using said composition and a treated article.

DETAILED EXPLANATION OF THE INVENTION

[0008] As the HLB value, adopted is a value shown in a brochure when the brochure shows the HLB value, and is a measured value (measured according to W. G. Griffin, J. Soc. Cosmetic Chemists, 1, 311 (1949) and W. G. Griffin, J. Soc. Cosmetic Chemists, 5, 249 (1954)) when brochures do not show an HLB value.

[0009] Specific examples of the nonionic surfactant used in the present Invention include polyoxyethylene lauryl ether, polyoxyethylene tridecyl ether, polyoxyethylene cetyl ether, polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene monolaurate, polyoxyethylene monostearate, polyoxyethylene mono-oleate, sorbitan monolaurate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monostearate, sorbitan mono-oleate, sorbitan sesquioleate, sorbitan trileate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan mono-oleate, polyoxyethylene polyoxypropylene block polymer, polyglycerin fatty acid ester, polyether-modified silicone oil (SH3746, SH3748, SH3749 and SH3771 manufactured by Toray Dow Corning Silicone Co., Ltd.), perfluoroalkyl ethylene oxide adduct (UNIDYNE DS-401 and DS-403 manufactured by Daikin Industries, Ltd.), fluoroalkyl ethylene oxide adduct (UNIDYNE DS-406 manufactured by Daikin Industries, Ltd.), and perfluoroalkyl oligomer (UNIDYNE DS-451 manufactured by Daikin Industries, Ltd.).

[0010] A preferable structure of the nonionic surfactant includes polyoxyethylene dialkylate, polyoxyethylene monoalkylate, polyoxyalkylene alkyl ether and sorbitan alkylate.

EP 1 365 000 A1

[0011] Most preferable specific examples of the nonionic surfactant include polyoxyethylene (POE) (8) distearate, polyoxyethylene (POE) (5) dilaurate, POE (2-6) monostearate, POE (6) monooleate, POE (3-5) alkyl ether and POE (2) cetyl ether.

[0012] The HLB value of the nonionic surfactant is at most 11, preferably at most 9.

5 [0013] An other nonionic surfactant having an HLB value of more than 11 may be used together with the nonionic surfactant having the HLB value of at most 11 (preferably at most 9), but the other nonionic surfactant preferably has the HLB value between 9 and 13, for example between 11 and 13.

10 [0014] When the combination of the nonionic surfactant having low HLB value and the nonionic surfactant having high HLB value is used, the amount of the nonionic surfactant having the HLB value of at most 9 is preferably at least 60% by weight, more preferably at least 80% by weight, based on the total of the nonionic surfactants. The nonionic surfactant having the HLB value of at most 9 alone may be used as the nonionic surfactant.

15 [0015] The amount of the nonionic surfactant having the HLB value of at most 11 (preferably at most 9) is from 0.1 to 100 parts by weight, based on 100 parts by weight of the polymer.

[0016] The nonionic surfactant is combinedly used together with the cationic surfactant. The cationic surfactant may be either a fluorine-containing cationic surfactant or a fluorine-free cationic surfactant.

20 [0017] Specific examples of the cationic surfactant used in the present invention include dialkyl (C₁₂-C₂₂) dimethyl ammonium chloride, alkyl (coconut) dimethyl benzyl ammonium chloride, octadecyl amine acetate salt, tetradecyl amine acetate salt, tallow alkyl propylene diamine acetate salt, octadecyl trimethyl ammonium chloride, alkyl (tallow) trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, alkyl (coconut) trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, biphenyl trimethyl ammonium chloride, alkyl (tallow) imidazoline quaternary salt, tetradecyl dimethyl benzyl ammonium chloride, octadecyl dimethyl benzyl ammonium chloride, dioleyl dimethyl ammonium chloride, polyoxyethylene dodecyl monomethyl ammonium chloride, polyoxyethylene alkyl (C₁₂-C₂₂) benzyl ammonium chloride, polyoxyethylene lauryl monomethyl ammonium chloride, 1-hydroxyethyl-2-alkyl (tallow) imidazoline quaternary salt, a silicone-based cationic surfactant having a siloxane group as a hydrophobic group, and a fluorine-based cationic surfactant having a fluoroalkyl group as a hydrophobic group (UNIDYNE DS-202 manufactured by Daikin Industries, Ltd.).

25 [0018] Preferable specific examples of the cationic surfactant are monoalkyltrimethyl ammonium salt and dialkyldimethyl ammonium salt. Most preferable specific examples include stearyltrimethyl ammonium chloride, lauryl trimethyl ammonium chloride, di-harden tallow alkyl dimethyl ammonium chloride and distearyl dimethyl ammonium chloride.

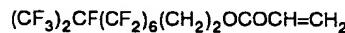
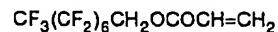
30 [0019] Non-limiting examples of the perfluoroalkyl group-containing ethylenically unsaturated monomer are as follows:

[0020] The perfluoroalkyl group-containing ethylenically unsaturated monomer is preferably a (meth)acrylate ester containing a perfluoroalkyl group. The perfluoroalkyl group-containing ethylenically unsaturated monomer is preferably of the formula:

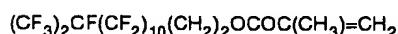
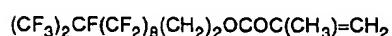
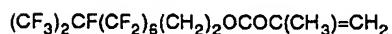
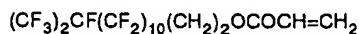
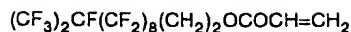


40 wherein Rf is a linear or branched perfluoroalkyl group having 3 to 20 carbon atoms; R¹ is a linear or branched alkylene group having 1 to 20 carbon atoms, a group of the formula: -SO₂N(R³)R⁴- or a group of the formula: -CH₂CH(OR⁵)CH₂- in which R³ is an alkyl group having 1 to 10 carbon atoms, R⁴ is a linear or branched alkylene group having 1 to 10 carbon atoms, and R⁵ is a hydrogen atom or an acyl group having 1 to 10 carbon atoms; and R² is a hydrogen atom or a methyl group.

45 [0021] Non-limiting specific examples of the monomer containing the perfluoroalkyl group are as follows:



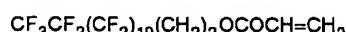
EP 1 365 000 A1



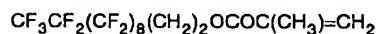
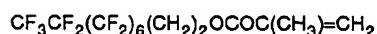
15



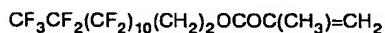
20



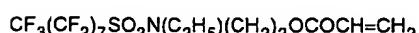
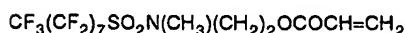
25



30



35



40



45

[0022] The perfluoroalkyl group-containing ethylenically unsaturated monomer may be a monomer having a urethane or urea bond and a fluoroalkyl group.

[0023] The monomer having the urethane or urea bond and the fluoroalkyl group may be, for example, a compound of the general formula:

50



wherein

55

R^{f1} is a linear or branched perfluoroalkyl group having 3 to 20 carbon atoms; X¹ is -R¹-, -CON(R²)-Q¹- or -SO₂N(R²)-Q¹-, in which R¹ is an alkylene group, R² is a hydrogen atom or a lower alkyl group and Q¹ is an alkylene group;

EP 1 365 000 A1

A¹ is -O-, -S- or -N(R²)-, in which R² is a hydrogen atom or a lower alkyl group;
Y¹ is a residue remaining after removing an isocyanate from an aromatic or alicyclic diisocyanate;
A² is a bivalent organic group having 2 to 9 carbon atoms and capable of containing at least one oxygen atom; and
R³ is a hydrogen atom or a methyl group.

- 5 [0024] The perfluoroalkyl group-containing ethylenically unsaturated monomer is particularly preferably CF₃CF₂(CF₂CF₂)_nCH₂CH₂OOCCH=CH₂ (n = 2 to 8).
10 [0025] The amount of the perfluoroalkyl group-containing ethylenically unsaturated monomer is from 40 to 100% by weight, preferably from 50 to 90% by weight, more preferably 55 to 85% by weight, based on the copolymer. If the perfluoroalkyl group-containing ethylenically unsaturated monomer is in a small amount, the water- and oil-repellency is not good.
15 [0026] Non-limiting examples of a comonomer copolymerizable with the perfluoroalkyl group-containing ethylenically unsaturated monomer are the following fluorine-free monomers, particularly fluorine-free functional group-containing monomers.
[0027] The fluorine-free monomer is preferably a diene monomer, a (meth)acrylate ester monomer or a di(meth)
acrylate ester monomer.
[0028] Specific examples of the diene monomer include butadiene, isoprene and chloroprene.
[0029] The (meth)acrylate ester monomer may be a compound of the formula:



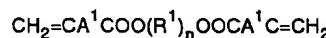
or



wherein

- 30 A¹ is a hydrogen atom or a methyl group,
A² is a C₁-C₃₀ linear or branched alkyl group,
R¹ is a C₁-C₆ linear or branched alkylene group, and
n is an integer of 1 to 30.

- 35 [0030] The di(meth)acrylate ester monomer may be a compound of the formula:



40 or



45 wherein

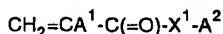
A¹ is a hydrogen atom or a methyl group,
R¹ is a C₁-C₆ linear or branched alkylene group, and
n is an integer of 1 to 30.

- 50 [0031] The homopolymer of the fluorine-free monomer has the glass transition temperature of at most 50°C.
[0032] Examples of the monomer having a glass transition temperature of 30 to 50°C include cetyl acrylate and isobutyl methacrylate for specific examples of the (meth)acrylate ester monomer; and polyethylene glycol(4) diacrylate for specific examples of the di(meth)acrylate ester monomer.
55 [0033] Examples of the monomer having a glass transition temperature of more than 0°C and less than 30°C include methyl acrylate, n-butyl methacrylate and cetyl methacrylate for specific examples of the (meth)acrylate ester monomer.
[0034] Examples of the monomer having a glass transition temperature of 0°C or less include isoprene and 1,3-butadiene for specific examples of the diene monomer; and ethyl acrylate, n-butyl acrylate, n-octyl acrylate, 2-ethylhexyl

(meth)acrylate and n-lauryl (meth)acrylate for specific examples of the (meth)acrylate ester monomer.

[0035] As the fluorine-free monomer, also suitable are C₂-C₁₄ alkyl (meth)acrylate, vinyl chloride (VCl), vinylidene chloride (VdCl), butadiene and chloroprene. The amount of the comonomer (the fluorine-free monomer) is preferably at most 60% by weight, more preferably at most 50% by weight, particularly preferably at most 45% by weight, based on the copolymer.

[0036] The copolymerizable fluorine-free functional group-containing monomer may be, for example, a compound of the formula:



wherein

A¹ is a hydrogen atom or a methyl group,

X¹ is -O-, -CH₂- or -NH-,

A² is a hydrogen atom, a hydrophilic group or a group containing a hydrophilic group.

[0037] Specific examples of the hydrophilic group in the fluorine-free functional group-containing monomer include a hydroxyl group, a glycidyl group, an ether group, an ester group, an amino group, a urethane group, a phosphate group and a sulfate group.

[0038] Specific examples of the fluorine-free functional group-containing monomer include glycidyl methacrylate, hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl acrylate, 2-hydroxyethyl acrylate, glycerol monomethacrylate, β-acryloyloxyethyl hydrogen succinate, β-methacryloyloxyethyl hydrogen phthalate, 2-acryloyloxyethylhexahydrophthalic acid, 2-acryloyloxyethylphthalic acid, 2-acryloyloxyethyl-2-hydroxyethylphthalic acid, hydroxypropyl methacrylate trimethylammonium chloride, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-acryloyloxyethyl acid phosphate, glucosylethyl methacrylate, methacrylamide, 2-acrylamido-2-methylpropanesulfonic acid, 2-hydroxy-3-acryloyloxypropyl methacrylate, 2-methacryloyloxyethyl acid phosphate and neopentyl glycol hydroxypivalate diacrylate.

[0039] Other examples of the fluorine-free functional group-containing monomer include 3-chloro-2-hydroxypropyl methacrylate, chloromethylstyrene, chlorostyrene, chloroethyl vinyl ether, tetrahydrofurfuryl (meth)acrylate and polyoxyethylene (meth)acrylate.

[0040] The amount of the fluorine-free functional group-containing monomer may be at most 20% by weight, preferably at most 15% by weight, more preferably at most 10% by weight, based on the copolymer.

[0041] The copolymer of the present Invention can be prepared by emulsion polymerization, solution polymerization, suspension polymerization or bulk polymerization. In particular, the emulsion polymerization is preferred. Monomers are emulsion-polymerized by use of water, an emulsifying agent and optionally an organic solvent. The mixture may previously be emulsified by a high-pressure emulsifying machine or the like before polymerization.

[0042] The emulsifying agent used may be any type of a surfactant, such as a cationic, anionic, nonionic or amphoteric surfactant. Examples of the cationic and nonionic surfactants are as mentioned above.

[0043] Specific examples of the anionic surfactant include sodium lauryl sulfate, lauryl sulfate triethanolamine, sodium polyoxyethylene lauryl ether sulfate, sodium polyoxyethylene nonyl phenyl ether sulfate, polyoxyethylene lauryl ether sulfate triethanolamine, sodium cocoyl sarcosine, sodium N-cocoyl methyl taurine, sodium polyoxyethylene cocount alkyl ether sulfate, sodium diether hexyl sulfosuccinate, sodium α-olefin sulfonate, sodium lauryl phosphate, sodium polyoxyethylene lauryl ether phosphate, and perfluoroalkyl carboxylate salt (UNIDYNE DS-101 and 102 manufactured by Daikin Industries, Ltd.).

[0044] Examples of the organic solvent used in the emulsion polymerization are as follows: Ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohols such as ethanol, isopropanol and butanol; polyhydric alcohols such as 1,3-butanediol, 1,6-hexanediol, ethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol and glycerol; ethers and esters of polyhydric alcohol such as dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, triethylene glycol dimethyl ether and diethylene glycol monobutyl ether acetate; esters such as ethyl acetate, propyl acetate, butyl acetate, dibutyl adipate and dibutyl succinate; hydrocarbon and halogenated hydrocarbon such as toluene, xylene, octane, perchloroethylene and 1,3-dichloro-2,2,3,3,3-pentafluoropropane.

[0045] The composition of the present invention can be prepared by emulsion-polymerizing the perfluoroalkyl group-containing ethylenically unsaturated monomer in the presence of the specified amounts of the nonionic surfactant having low HLB and the cationic surfactant.

[0046] Alternatively, the composition of the present invention can be prepared by emulsion-polymerizing the perfluoroalkyl group-containing ethylenically unsaturated monomer in the presence of either the nonionic surfactant having low HLB or the cationic surfactant, and then adding the surfactants to give the specified amounts of the nonionic

EP 1 365 000 A1

surfactant having low HLB and the cationic surfactant.

[0047] In addition to the above-mentioned copolymer, surfactant and solvent, the composition of the present invention may contain various additives such as softening agents, cross-linking agents, antistatic agents, flame-retardants and anti-microbial agents.

5 [0048] The composition of the present invention can be applied to a substrate according to a conventionally known method. A method of dispersing the composition into water to dilute it, attaching it on the substrate by a procedure such as dip application, spray application and coat application to the substrate, and drying and/or heat-treating it is usually adopted. The temperature of curing is generally from 80°C to 180°C, particularly from 80°C to 140°C.

10 [0049] The concentration of the copolymer is generally from 0.1% to 70% by weight, based on the composition of the present invention. When the composition is diluted with and dispersed in water, the concentration of the copolymer in the treatment liquid may be from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight.

[0050] When the substrate is dried and/or heat-treated, the temperature may be at least 150°C, but the temperature limited in view of the heat resistance of the substrate may be at most 140°C, particularly from 80°C to 120°C so as to give sufficient properties.

15 [0051] The substrate (or article) to be treated with the composition of the present invention is preferably a textile. As the textile, various examples can be mentioned. Examples of them include a natural fiber such as cotton, hemp, silk and wool; a synthetic fiber such as a polyamide, a polyester, polyacrylonitrile, polyvinyl chloride and polypropylene; a semi-synthetic fiber such as rayon and acetate; an inorganic fiber such as glass fiber, carbon fiber and asbestos fiber; and a mixture of these fibers. Because the composition of the present invention has the characteristics of exhibiting sufficient properties after drying and/or heat treatment even at not higher than 140°C, it can be effectively applied to a fiber of polyolefin having poor heat resistance, such as polypropylene and polyethylene.

[0052] The textile may be any of in the form of yarn, fabric and the like.

[0053] Examples of the substrate which can be treated with the composition of the present invention include glass, paper, wood, leather, fur, metal and plastics, in addition to the textile.

25 [0054] The substrate treated with the composition of the present invention can be used in various uses and is not limited. The composition of the present invention can be effectively used in furniture applications, and medical and sanitary applications using polyolefin fibers such as polypropylene fibers and polyethylene fibers, and textile blends thereof which can not obtain sufficient performances by conventional technologies.

30 PREFERRED EMBODIMENTS OF THE INVENTION

[0055] The following Examples and Comparative Examples, which do not limit the present invention, further illustrate the present invention in detail. In the Examples and Comparative Examples, "%" is "% by weight" unless otherwise specified.

35 [0056] The properties are measured as follows.

Water repellency

40 [0057] Aqueous solution of Isopropyl alcohol (IPA) shown in Table 1 is positioned on a test fabric, the water-repellency is evaluated according to AATCC-TM118-1992 and then expressed as water-repellency grade shown in Table 1.

Table 1

	Water repellency grade	Test liquid (volume ratio %)
45	10	IPA 100
	9	IPA 90/water 10
	8	IPA 80/water 20
	7	IPA 70/water 30
	6	IPA 60/water 40
	5	IPA 50/water 50
	4	IPA 40/water 60
50	3	IPA 30/water 70
	2	IPA 20/water 80
	1	IPA 10/water 90
	W	Water 100
	0	Inferior to W

Oil-repellency

5 [0058] According to AATCC-TM118-1992, several droplets (diameter: 4mm) of the test liquid shown in Table 2 are positioned on two sites of test fabric, and penetration states of the test liquid are determine after 30 seconds. The oil-repellency is expressed by the oil-repellency grade shown in Table 2.

Table 2

	Oil repellency grade	Test solution	Surface tension (dyne/cm, 25°C)
10	8	n-Heptane	20.0
	7	n-Octane	21.3
	6	n-Decane	23.5
	5	n-Dodecane	25.0
	4	n-Tetradecane	26.7
	3	n-Hexadecane	27.3
	2	Mixture of n-hexadecane/nujol (35/65)	29.6
	1	Nujol	31.2
20	0	Inferior to 1	-

Preparative Example 1 (Preparation of water-based water- and oil-repellent agent)

25 [0059] A monomer [70 g of perfluoroalkyl ethyl acrylate (FA) [$C_nF_{2n+1}CH_2CH_2COOCH=CH_2$] (a mixture of compounds wherein n is 6, 8, 10, 12 and 14 (average of n is 9))], 25 g of lauryl acrylate (LA), 2.5 g of N-methylol acrylamide (N-MAM) and 2.5 g of 3-chloro-2-hydroxypropyl methacrylate (CHPMA)], an emulsifying agent [2 g of di-harden tallow alkyl dimethyl ammonium chloride (cationic surfactant A), 2 g of lauryl trimethyl ammonium chloride (cationic surfactant B) and 7 g of polyoxyethylene(8) distearate (nonionic surfactant An HLB value: 8.5)], a solvent (30 g of tripropylene glycol (TPG)), a chain transfer agent (0.5 g of dodecyl mercaptan) and 191 g of water were charged, mixed with a homomixer and then emulsified with an ultrasonic emulsifier. The flask was replaced with nitrogen, an initiator (0.6 g of 2,2'-azobis (2-amidinopropane) dihydrochloride) was added and the polymerization was conducted at 60°C over 4 hours. The disappearance of the monomers was confirmed by GC. The resultant water- and oil-repellent composition had a solid content (residue after evaporation at 130°C over 2 hours) of 33%.

30 35 Preparative Examples 2 to 14 and Comparative Preparative Examples 1 to 3
(Preparation of water-based water- and oil-repellent agent)

40 [0060] Types and amounts of monomers and emulsifying agents shown in Table A were used in the same manner as in Preparative Example 1 to give a water- and oil-repellent composition.

Preparative Example 15 (Preparation of water-based water- and oil-repellent agent)

45 [0061] A monomer [70 g of perfluoroalkylethyl acrylate (FA) [$C_nF_{2n+1}CH_2CH_2COOCH=CH_2$] (a mixture of compounds wherein n is 6, 8, 10, 12 and 14 (average of n is 9))], 20 g of lauryl acrylate (LA), 2.5 g of N-methylol acrylamide (N-MAM) and 2.5 g of 3-chloro-2-hydroxypropyl methacrylate (CHPMA)], an emulsifying agent [2 g of di-harden tallow alkyl dimethyl ammonium chloride (cationic surfactant A), 2 g of lauryl trimethyl ammonium chloride (cationic surfactant B), 5 g of polyoxyethylene(8) distearate (nonionic surfactant An HLB value: 8.5) and branched primary lauryl alcohol POP(6) POE(20) adduct (nonionic surfactant L, HLB value: 12.3)], a solvent (30 g of tripropylene glycol (TPG)), a chain transfer agent (0.5 g of dodecyl mercaptan) and 191 g of water were charged, mixed with a homomixer and then emulsified with an ultrasonic emulsifier. The emulsified liquid was charged into an autoclave and degassed to vacuum, and 7.1 g of a vinyl chloride monomer was charged. An initiator (0.6 g of 2,2'-azobis(2-amidinopropane) dihydrochloride) was added to conduct the polymerization at 60°C over 4 hours. After the completion of the polymerization, unreacted vinyl chloride monomer was removed off (The conversion of the vinyl chloride monomer was 70%). The disappearance of the other monomers was confirmed by GC. The resultant water- and oil-repellent composition had a solid content (residue after evaporation at 130°C over 2 hours) of 33%.

S 22081

EP 1 365 000 A1

Preparative Examples 16 to 19 (Preparation of water-based water- and oil-repellent agent)

[0062] Types and amounts of monomers and emulsifying agents shown in Table B were used in the same manner as in Preparative Example 15 to give a water- and oil-repellent composition.

5

Example 1

[0063] The water- and oil-repellent composition obtained in Preparative Example 1 was diluted with water to give a water- and oil-repellent treatment liquid having a solid content of 0.5%. A cotton fabric (broad) and a polypropylene (PP) fabric (twill weave) were dipped into this treatment liquid and squeezed with rolls. The wet pick up was 65% for the cotton fabric and 75% for the PP fabric. These treated fabrics were dried with a pin tenter at 120°C for 3 minutes. Then the water- and oil-repellency test was conducted. The test results are shown in Table A.

10

Examples 2 to 19 and Comparative Examples 1 to 3

15

[0064] The water- and oil-repellent composition obtained in Preparative Examples 2 to 19 and Comparative Preparative Examples 1 to 3 was subjected to the water- and oil-repellency test as in Example 1. Test results are shown in Table A.

20

Preparative Example 20 (Preparation of water-based water- and oil-repellent agent)

[0065] The composition obtained in Comparative Preparative Example 2 was diluted with water to a solid content of 0.5%, and polyoxyethylene(8) distearate (nonionic surfactant An HLB value: 8.5) in the amount of 0.1 % relative to the diluted liquid was added to give a water- and oil-repellent composition.

25

Preparative Examples 21 to 28 and Comparative Preparative Examples 5 and 6

(Preparation of water-based water- and oil-repellent agent)

30

[0066] In the same manner as in Preparative Example 20, the composition obtained in Comparative Preparative Example 2 was diluted with water to a solid content of 0.5%, a nonionic surfactant shown in Table C in the amount of 0.3% relative to the diluted liquid was added to give a water- and oil-repellent composition.

Example 20

35

[0067] The water- and oil-repellent composition obtained in Preparative Example 20 as such was used as a water- and oil-repellent treatment liquid. A cotton fabric (broad) and a polypropylene (PP) non-woven fabric were dipped into this treatment liquid and squeezed with rolls. The wet pick up was 65% for the cotton fabric and 170% for the PP non-woven fabric. These treated fabrics were dried with a pin tenter at 80°C for 5 minutes. Then the water- and oil-repellency test was conducted. The test results are shown in Table C.

Examples 21 to 28 and Comparative Examples 5 and 6

40

[0068] The water- and oil-repellent composition obtained in Preparative Examples 19 to 26 and Comparative Preparative Examples 5 and 6 was subjected to the water- and oil-repellency test as in Example 20. Test results are shown in Table C.

Comparative Example 4

45

[0069] The water- and oil-repellent composition obtained in Comparative Preparative Example 2 was diluted with water to a solid content of 0.5%, and the diluted liquid as such was used as a water- and oil-repellent treatment liquid. The water- and oil-repellency test was conducted as in Example 20. Test results are shown in Table C.

Example 29

50

[0070] The water- and oil-repellent composition obtained in Preparative Example 1 was diluted with water to give a water- and oil-repellent treatment liquid having a solid content of 0.5%. A propylene (PP) fabric for furniture (weight per unit area of fabric: 197 g/m²), a propylene (PP)/cotton union fabric for furniture (weight per unit area of fabric: 380

EP 1 365 000 A1

g/m²), a cotton fabric for furniture (weight per unit area of fabric: 235 g/m²) and a propylene non-woven fabric for medical use (weight per unit area of fabric: 40 g/m²) were dipped into this treatment liquid and squeezed with rolls. These treated fabrics were dried with a pin tenter and the water- and oil-repellency test was conducted. The wet pick up and drying conditions were 64%; 100°C and 3 minutes for the furniture use PP fabric; 67%; 80°C and 6 minutes for the furniture use PP/cotton union fabric; 71%; 80°C and 3 minutes for the furniture use cotton fabric; and 130%; 90°C and 2 minutes for the medical use PP non-woven fabric. The test results are shown in Table D.

5 Comparative Preparative Example 7

10 [0071] Types and amounts of monomers and emulsifying agents shown in Table D were used in the same manner as in Preparative Example 1 to give a water- and oil-repellent composition.

15 Comparative Example 7

15 [0072] The water- and oil-repellent composition obtained in Comparative Preparative Example 7 was subjected to the water- and oil-repellency test as in Example 29. Test results are shown in Table D.

20

25

30

35

40

45

50

55

Table A

	HLB	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FA		70	70	70	70	70	70	70	70	70	70	70	70	70	70
LA		25	25	25	25	25	25	25	25	25	25	25	25	25	25
2EHA		-	-	-	-	-	-	-	-	-	-	-	-	-	-
N-MAM		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CHPMA		2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CMS		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cationic surfactant A		2	2	2	2	2	2	2	2	2	2	2	2	2	2
Cationic surfactant B		2	2	2	2	2	2	2	2	2	2	2	2	2	2
Nonionic surfactant A	8.5	7													
Nonionic surfactant B	9.5	7													
Nonionic surfactant C	8.0		7												
Nonionic surfactant D	10.5			7											
Nonionic surfactant E	8.0				7										
Nonionic surfactant F	7.5					7									
Nonionic surfactant G	8.6						7								
Nonionic surfactant H	4.0							7							
Nonionic surfactant I	6.5								7						
Nonionic surfactant J	8.5									7					
Nonionic surfactant K	11.0										7				
Nonionic surfactant L	12.3											7			
PP fabric (twill)															
Water-repellency (IPA/water)	9	8	9	9	9	9	9	9	9	9	9	9	9	9	9
Oil-repellency	4	3	4	3	4	4	3	4	3	4	3	3	4	4	4
Cotton fabric (broad)															
Water-repellency (IPA/water)	7	6	6	6	6	6	6	6	5	5	5	6	6	7	7
Oil-repellency	4	4	4	4	3	3	3	3	3	3	3	4	4	4	4

Note)

5	FA:	Perfluoroalkylethyl acrylate
	LA:	Lauryl acrylate
	2EHA:	2-Ethylhexyl acrylate
10	N-MAM:	N- Methylol acrylamide
	CHPMA:	2-Hydroxy-3-chloropropyl methacrylate
	CMS:	Chloromethylstyrene
	Cationic surfactant A:	Di-harden tallow alkyl dimethyl ammonium chloride
	Cationic surfactant B:	Lauryl trimethyl ammonium chloride
15	Nonionic surfactant A:	POE(8) distearate
	Nonionic surfactant B:	POE(8) diisostearate
	Nonionic surfactant C:	POE(3) secondary alkyl ether
	Nonionic surfactant D:	POE(5) secondary alkyl ether
20	Nonionic surfactant E:	POE(2) cetyl ether
	Nonionic surfactant F:	POE(2) oleyl ether
	Nonionic surfactant G:	Sorbitan monolaurate
	Nonionic surfactant H:	POE(2) monostearate
25	Nonionic surfactant I:	POE(4) monostearate
	Nonionic surfactant J:	POE(6) monooleate
	Nonionic surfactant K:	POE(10) monostearate
30	Nonionic surfactant L:	Branched primary lauryl alcohol POP(6) POE(20) adduct

35

40

45

50

55

Table B

		HLB	15	16	17	18	19	Comparative Example
FA		70	80	80	80	80	70	70
StA		-	-	-	-	-	-	25
LA		20	-	-	-	-	25	-
VCI		5	15	-	-	-	-	-
VdCl		-	-	15	-	-	-	-
Butadiene		-	-	-	15	-	-	-
Chloroprene		-	-	-	-	15	-	-
N-MAM		2.5	2.5	2.5	2.5	2.5	2.5	2.5
CHPMA		2.5	2.5	2.5	2.5	2.5	2.5	2.5
Cationic surfactant A		2	2	2	2	2	2	-
Cationic surfactant C		-	-	-	-	-	-	2
Cationic surfactant B		2	2	2	2	2	2	-
Nonionic surfactant A	8.5	5	5	5	5	5	-	-
Nonionic surfactant L	12.3	2	2	2	2	2	-	-
Nonionic surfactant M	15.0	-	-	-	-	7	-	-
Nonionic surfactant N	16.2	-	-	-	-	-	7	-
PP fabric (twill)								
Water-repellency (IPA/water)	10	8	8	8	8	5	3	4
Oil-repellency	4	3	3	3	3	0	0	1
Cotton fabric (flamed)								
Water-repellency (IPA/water)	6	5	5	5	5	4	3	3
Oil-repellency	4	5	4	4	4	3	1	2

EP 1 365 000 A1

Note)

- 5 StA: Stearyl acrylate
VCl: Vinyl chloride
VdCl: Vinylidene chloride
Nonionic surfactant A: POE(8) distearate
10 Nonionic surfactant L: Branched primary lauryl alcohol POP(6) POE(20) adduct
Nonionic surfactant M: POE(25) monostearate
Nonionic surfactant N: POE(20) octylphenyl ether
Cationic surfactant A: Di-harden tallow alkyl dimethyl ammonium chloride
15 Cationic surfactant B: Lauryl trimethyl ammonium chloride
Cationic surfactant C: Stearyl trimethyl ammonium chloride

20

25

30

35

40

45

50

55

Table C

Composition of Preparative Example 2	HLB	Example						Comparative Example				
		20	21	22	23	24	25	26	27	28	4	5
Nonionic surfactant A	8.5	0.1	0.3								0.5	0.5
Nonionic surfactant B	9.5										0.5	0.5
Nonionic surfactant J	8.5										0.5	0.5
Nonionic surfactant C	8.0										0.5	0.5
Nonionic surfactant D	10.5										0.5	0.5
Nonionic surfactant E	8.0										0.5	0.5
Nonionic surfactant F	7.5										0.5	0.5
Nonionic surfactant G	8.6										0.5	0.5
Nonionic surfactant O	16.5										0.5	0.5
Nonionic surfactant M	15.0										0.5	0.5
PP non-woven fabric												
Water-repellency (IPA/water)	6	9	8	9	10	7	9	9	9	3	3	3
Oil-repellency	2	4	3	3	5	2	3	3	2	0	0	0
Cotton fabric (broad)												
Water-repellency (IPA/water)	4	5	4	4	4	3	4	4	3	2	0	0
Oil-repellency	3	3	2	2	3	2	3	3	2	1	0	0

EP 1 365 000 A1

Note)

- 5 Nonionic surfactant A: POE(8) distearate
 Nonionic surfactant B: POE(8) diisostearate
 Nonionic surfactant J: POE(6) monooleate
 10 Nonionic surfactant C: POE(3) secondary alkyl ether
 Nonionic surfactant D: POE(5) secondary alkyl ether
 Nonionic surfactant E: POE(2) cetyl ether
 Nonionic surfactant F: POE(2) oleyl ether
 Nonionic surfactant G: Sorbitan monolaurate
 15 Nonionic surfactant O: POE(150) distearate
 Nonionic surfactant M: POE(25) monostearate

Table D

	HLB	Example 29	Comparative Example 7
FA		70	70
LA		25	-
StA		-	25
N-MAM		2.5	2.5
CHPMA		2.5	2.5
Cationic surfactant A		2	-
Cationic surfactant B		2	-
Cationic surfactant C		-	3
Nonionic surfactant A	8.5	7	-
Nonionic surfactant N	16.2	-	7
Furniture use PP fabric			
Water-repellency(IPA/water)		7	2
Oil-repellency		4	1
Furniture use PP/cotton union fabric			
Water-repellency(IPA/water)		10	0
Oil-repellency		6	0
Furniture use cotton fabric			
Water-repellency(IPA/water)		10	0
Oil-repellency		7	0
Medical use PP non-woven fabric			
Water-repellency(IPA/water)		9	2
Oil-repellency		3	0

EFFECTS OF THE INVENTION

- 55 [0073] The aqueous dispersion type fluorine-containing water- and oil-repellent agent of the present invention has excellent water- and oil-repellency performances when cured at low temperature.

EP 1 365 000 A1

Claims

- 5 1. An aqueous dispersion type fluorine-containing water- and oil-repellent composition comprising a polymer of a perfluoroalkyl group-containing ethylenically unsaturated monomer dispersed in an aqueous medium, wherein the composition contains a nonionic surfactant having an HLB value of at most 11 and a cationic surfactant, and a homopolymer of at least one monomer constituting the polymer has a glass transition temperature (Tg) of at most 50°C.
- 10 2. An aqueous dispersion type fluorine-containing water- and oil-repellent composition comprising a polymer of a perfluoroalkyl group-containing ethylenically unsaturated monomer dispersed in an aqueous medium, wherein the composition contains a nonionic surfactant having an HLB value of at most 11 and a cationic surfactant, and at least one monomer constituting the polymer is one or at least two selected from C₂-C₁₄ alkyl (meth)acrylate, vinyl chloride (VCl), vinylidene chloride (VdCl), butadiene and chloroprene.
- 15 3. The composition according to claim 1 or 2, wherein the nonionic surfactant has the HLB value of at most 9.
- 20 4. The composition according to claim 3, wherein the composition contains a nonionic surfactant having the HLB value of 9 to 13 in addition to the nonionic surfactant having the HLB value of at most 9.
- 25 5. The composition according to claim 4, wherein the amount of the nonionic surfactant having the HLB value of at most 9 is at least 60% by weight, based on the total of the nonionic surfactant.
- 30 6. The composition according to anyone of claims 1 to 5, wherein the cationic surfactant is at least one selected from monoalkyl trimethyl ammonium salt and dialkyl dimethyl ammonium salt.
- 35 7. The composition according to anyone of claims 1 to 6, wherein the nonionic surfactant is at least one selected from polyoxyalkylenedialkyl ester, polyoxyalkylenealkyl ester, polyoxyalkylenealkyl ether and sorbitan alkyl ester.
- 40 8. The composition according to anyone of claims 1 to 7, wherein the amount of the nonionic surfactant is from 0.1 to 100 parts by weight, based on 100 parts by weight of the polymer.
- 45 9. A method of producing the aqueous dispersion type fluorine-containing water- and oil-repellent composition according to anyone of claims 1 to 8, wherein a monomer is polymerized in the presence of the nonionic surfactant having the HLB value of at most 11 and the cationic surfactant by an emulsion polymerization process to give a polymer.
- 50 10. A method of producing the composition according to anyone of claims 1 to 8, wherein the perfluoroalkyl group-containing ethylenically unsaturated monomer is polymerized in the presence of a surfactant and then the nonionic surfactant having the HLB value of at most 11 is added.
11. A treatment method comprising treating a textile with the composition according to anyone of claims 1 to 8 and then drying and/or heat-treating the textile.
12. The treatment method according to claim 11, wherein the drying and/or heat-treatment is conducted at at most 140°C.
13. An article treated with the method according to claim 11.
14. The article according to claim 13, wherein the article is a polyolefin fiber.
15. The article according to claim 13, wherein the article is for furniture use, or for medical or sanitary use.

INTERNATIONAL SEARCH REPORT		International application No. PCT/JP02/00624
A. CLASSIFICATION OF SUBJECT MATTER Int.Cl' C09K3/18, C08F2/24, D05M15/277		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl' C09K3/18, C08F2/24, D05M15/277		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 818506 A1 (DAIKIN INDUSTRIES, LIMITED), 14 January, 1998 (14.01.1998), Example 1-4 & JP 8-269285 A examples 1 to 4	1-15
A	EP 902073 A2 (Nippon Mektron, Limited), 17 March, 1999 (17.03.1999), Claim1, Par. No. [0030] & JP 11-80710 A Par. No. [0030]	1-15
A	JP 6-33043 A (Asahi Glass Co., Ltd.), 08 February, 1994 (08.02.1994), Par. No. [0040] (Family: none)	1-15
A	WO 00/43462 A1 (ASAHI GLASS COMPANY, LIMITED), 27 July, 2000 (27.07.2000), Claim 1 & JP 2000-212549 A Claim 1	1-15
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 19 February, 2002 (19.02.02)	Date of mailing of the international search report 05 March, 2002 (05.03.02)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)